Classical Motion

There are several formulations of classical mechanics:

- Newtonian : $F = ma$
- Lagrangian
- Hamiltonian

] in general these are easier to implement for many body systems

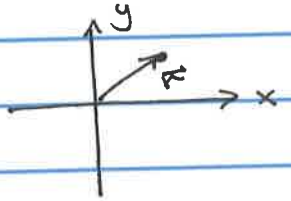
We're only going to talk briefly about this topic, and we'll assume conservative forces for now: $\vec{F} = -\vec{\nabla} U(\vec{r})$

(forces are the gradient of a scalar potential)

That is,

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = m_i \ddot{\vec{r}}_i = \vec{F}_i$$

Consider a 2D particle moving in a central force:



$$\vec{F} = -f(r)\,\hat{r}$$ ← unit vector

- force is always radially directed
- force is a function of distance from the origin

$$m\ddot{x} = \vec{F}\cdot\hat{\imath} = -f(r)\,x = -x f\left(\sqrt{x^2+y^2}\right)$$
$$m\ddot{y} = \vec{F}\cdot\hat{\jmath} = -f(r)\,y = -y f\left(\sqrt{x^2+y^2}\right)$$

Because the forces couple the two coordinates, other (polar) coordinates are more natural & useful

Polar coordinates require adding additional terms!

$$\begin{cases} mr^2\dot{\theta} = l & \leftarrow \text{constant angular momentum} \\ m\ddot{r} = -f(r) + \underbrace{\dfrac{l^2}{mr^3}} & \end{cases}$$

↑ fictitious "centrifugal" force

Lagrangian mechanics is indepent of coordinate system

$\vec{q}$ = vector of all coordinates

$\dot{\vec{q}}$ = vector of all velocities

$K(\vec{q}, \dot{\vec{q}})$ = kinetic energy, usually: $K = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{q}_i^2$

$U(\vec{q})$ = potential energy ← our force field!

$L(\vec{q}, \dot{\vec{q}})$ = "Lagrangian" = $K(\vec{q}, \dot{\vec{q}}) - U(\vec{q})$

$$\boxed{\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0}$$

← Lagrange's equation of motion, equivalent to F=ma

⇵ usually this gives us N 2nd order differential equations (one for each degree of freedom)

Example: $K = \frac{1}{2} m \dot{q}^2$ $U = \frac{1}{2} k q^2$

⇵ Harmonic oscillator

$$L = \frac{1}{2} m \dot{q}^2 - \frac{1}{2} k q^2$$

$$\frac{\partial L}{\partial \dot{q}} = m\dot{q} \qquad \frac{\partial L}{\partial q} = -kq$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \frac{\partial L}{\partial q} = 0$$

$$\frac{d}{dt}(m\dot{q}) - (-kq) = 0$$

$$\boxed{m\ddot{q} + kq = 0}$$

← solving a 2nd order diff EQ is generally difficult

Hamiltonian formulation

N 2nd order diff EQs become 2N 1st order diff EQs

Newton & Lagrange: q is primary
$\dot{q}$ is shorthand for $\frac{dq}{dt}$

Hamilton: q & p are both primary!

The Hamiltonian: $\mathcal{H} = K + U$

(more formally: $\mathcal{H} = L - \sum_i \dot{q}_i p_i$)

$$\boxed{\begin{aligned} \dot{q}_i &= \frac{\partial \mathcal{H}}{\partial p_i} \\ \dot{p}_i &= \frac{-\partial \mathcal{H}}{\partial q_i} \end{aligned}}$$ ← Hamilton's equations of motion

Σ

If we have a bunch of particles, each with position $\vec{r}_i$ and momentum $\vec{p}_i$, these give us simple 1st order equations to move $\vec{r}_i$ & $\vec{p}_i$

$$\frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i}{m} \qquad \frac{d\vec{p}_i}{dt} = \vec{F}_i = \underbrace{-\frac{\partial}{\partial \vec{r}_i} U(\vec{r})}_{\text{force field!}}$$

Let's take apart the derivatives

$$\frac{r_i(t+\Delta t) - r_i(t)}{\Delta t} = \frac{p_i(t)}{m} \qquad \frac{p_i(t+\Delta t) - p_i(t)}{\Delta t} = F_i(t)$$

So:

$$r_i(t+\Delta t) = r_i(t) + \Delta t \frac{p_i(t)}{m} \quad \& \quad p_i(t+\Delta t) = p_i(t) + \Delta t F_i(t)$$

Σ This is a primitive integrator of Hamilton's Equations!

Last Time:

Hamilton's Equations of Motion gave us 2 Differential Equations

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$$
$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

& conservative forces

For atoms in cartesian coordinates, we can write these in a form with velocities & forces:

$$\frac{d\vec{r}_i}{dt} = \vec{V}_i(t)$$

$$\frac{d\vec{V}_i}{dt} = \frac{\vec{F}_i[\vec{r}_i(t)]}{m_i}$$

← these forces are dependent on where the atoms are!

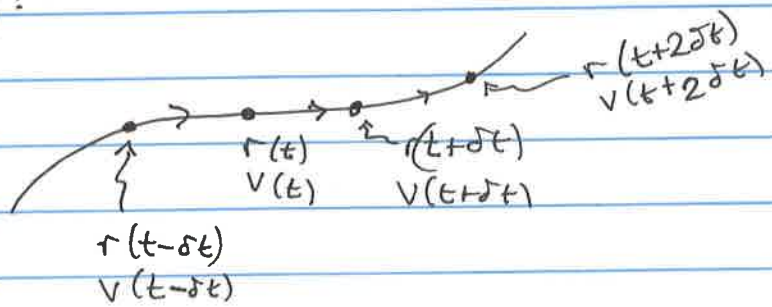
← Potential energy surface

$$\vec{F}[\vec{r}(t)] = -\nabla U(\vec{r}(t))$$

$$= -\begin{pmatrix} \partial U/\partial x_i \\ \partial U/\partial y_i \\ \partial U/\partial z_i \end{pmatrix}$$

← coordinates of all the atoms at time t.

We want to go from these diff EQs to a trajectory:



Integrators

What we'd like:

- minimize the number of calculations of F ← expensive!
- good stability at large Δt
- good accuracy
- conserves total energy & linear momentum
- time-reversible
- symplectic

} we'll come back to these two

Verlet integration

Let's briefly Taylor expand around t:

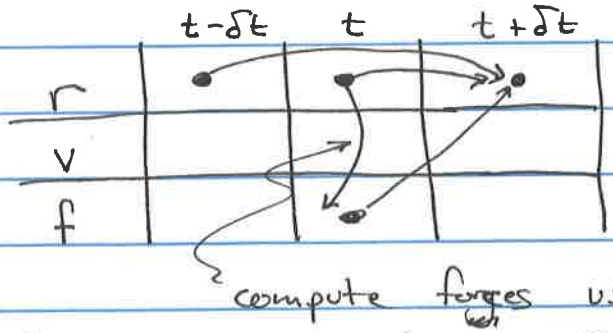
$$r(t+\delta t) = r(t) + \frac{p(t)}{m}\delta t + \frac{F(t)}{2m}\delta t^2 + \frac{1}{3}\dddot{r}(t)\delta t^3 + O(\delta t^4)$$

$$r(t-\delta t) = r(t) - \frac{p(t)}{m}\delta t + \frac{F(t)}{2m}\delta t^2 - \frac{1}{3}\dddot{r}(t)\delta t^3 + O(\delta t^4)$$

$$r(t+\delta t) + r(t-\delta t) = 2r(t) + \frac{F(t)}{m}\delta t^2 + O(\delta t^4)$$

$$\boxed{r(t+\delta t) = 2r(t) - r(t-\delta t) + \frac{F(t)}{m}\delta t^2 + O(\delta t^4)}$$

↑ "Position" Verlet integrator. It never uses p!



← propagating forward in time uses positions at two times + f(t)

compute forces using positions @ time t

If we want velocities @ time t, we can compute them after the step:

$$v(t) = \frac{1}{2\delta t}\left[r(t+\delta t) - r(t-\delta t)\right] + O(\delta t^2)$$

Leapfrog Verlet

① $v(t+\frac{\delta t}{2}) = v(t-\frac{\delta t}{2}) + \frac{F[r(t)]}{m}\delta t$

② $r(t+\delta t) = r(t) + v(t+\frac{\delta t}{2})\delta t$

↳ note that r & v are shifted by half a time step!

If we plug ① into ②:

$$r(t+\delta t) = r(t) + \left[v(t-\frac{\delta t}{2}) + \frac{F[r(t)]}{m}\delta t \right]\delta t$$

↳ But from the previous step:

$$r(t) = r(t-\delta t) + v(t-\frac{\delta t}{2})\delta t$$

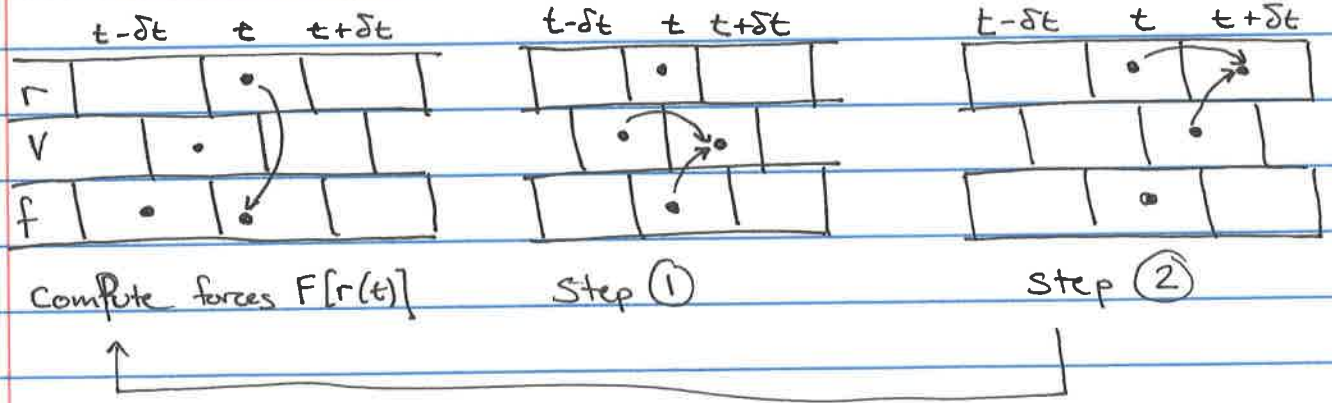
So we get

$$r(t+\delta t) = 2r(t) - r(t-\delta t) + \frac{F[r(t)]}{m}\delta t^2$$

↳ Leapfrog is formally equivalent to position Verlet

Instead of storing positions @ 2 different times, we store position & velocity at 2 different times.

Flow of Leapfrog Verlet:



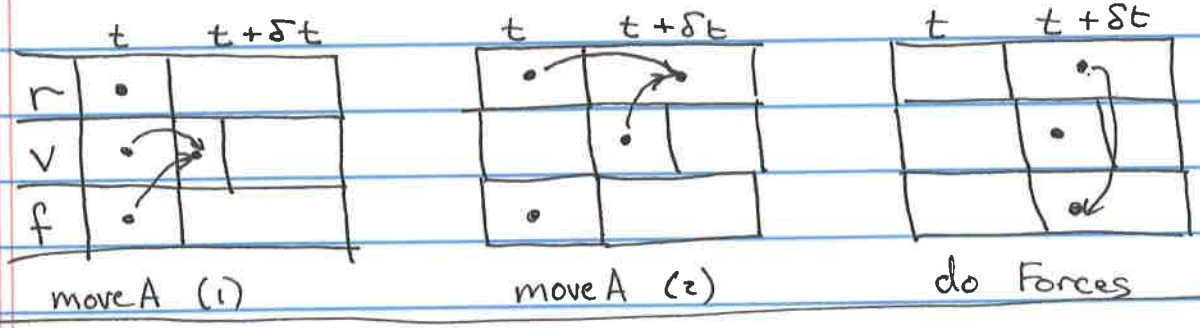
Current information always has r & v at ½ δt separation from each other

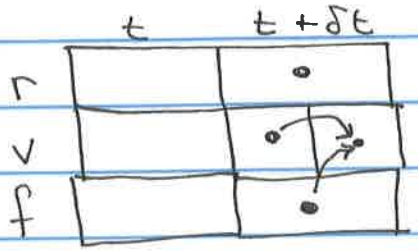
Velocity Verlet

move A : $\begin{cases} v\left(t+\frac{\delta t}{2}\right) = v(t) + \frac{F[r(t)]}{2m}\delta t \\ r(t+\delta t) = r(t) + v\left(t+\frac{\delta t}{2}\right)\delta t \end{cases}$

do Forces : $F[r(t+\delta t)]$

move B : $v(t+\delta t) = v\left(t+\frac{\delta t}{2}\right) + \frac{F[r(t+\delta t)]}{2m}\delta t$





← At the end of a step we have r, v, and f all at the same point in time

If we combine these steps, velocity verlet can also be written:

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{1}{2m}F(r(t)]\delta t^2$$

$$v(t+\delta t) = v(t) + \frac{1}{2m}\left(F[r(t)] + F[r(t+\delta t)]\right)\delta t$$

Velocity Verlet is now the standard method for MD.

It is:

- remarkably stable
- time reversible
- symplectic
- simple to code
- gives position & velocity information simultaneously
- light on Storage.

Other Methods

- Predictor - Corrector (not reversible)
- Runge - Kutta ← 4th order or higher
  - This method uses r', r'', r''', r'''' which are computed numerically.
  - requires more storage, and although timesteps can be longer, the additional expense can be large.

Dynamical Questions (What do we want to know?)

- How does the system respond collectively to stress?
- Conserved Quantities: mass, linear momentum, energy (where does it go & how quickly?)
- Non-conserved Quantities
  How quickly do they appear & vanish?
  Spectroscopy
- What do we need to compute to compare to experiments?

Balance Equations (conservation)

$$\frac{\partial c(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot\vec{j} = 0$$

$\frac{\partial c}{\partial t}$: change in concentration; $\vec{j}$: diffusive flux

Mass

$$c_p \frac{\partial T(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot\vec{q} = 0$$

$\vec{q}$: heat flux

Energy

$$\rho \frac{D\vec{v}(\vec{r},t)}{Dt} + \nabla\cdot\tau = 0$$

$\vec{v}$ = flow velocity; τ: stress tensor

Momentum

Constitutive Equations (Empirical Laws)

$$\vec{j} = -D\,\vec{\nabla}c(\vec{r},t)$$

D: Diffusion Const

Fick's Law

$$\vec{q} = -\lambda \nabla T$$

λ: thermal conductivity

Fourier's Law

$$\tau_{xy} = -\nu \nabla_y (\rho v_x)$$

Newton's Law of Viscosity

This symbol: $\frac{D}{Dt} = \frac{\partial}{\partial t} + \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$

is called a substantial or material derivative.

We can combine the Balance & Constitutive Equations.

For example, Mass Balance & Fick's Law give us:

$$\frac{\partial c(\vec{r},t)}{\partial t} - D\nabla^2 c(\vec{r},t) = 0$$

← $c(\vec{r},t)$ is the concentration of a solute at position $\vec{r}$ & time t.

↑ D is a physical property of the material

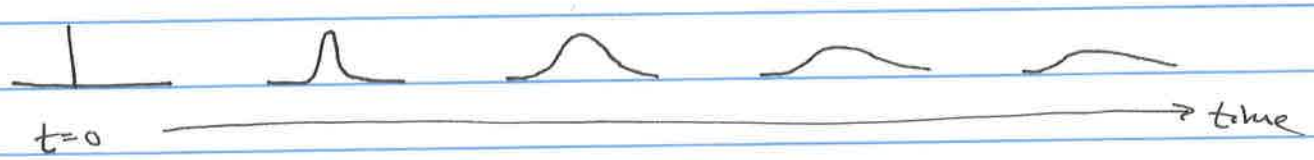
If we start an experiment with the solute all located at one point:

$$c(\vec{r},0) = \delta(\vec{r})$$ ← all solute at the origin

The solution of the combined equation — dimensionality

$$c(\vec{r},t) = (2\pi D t)^{-d/2} e^{-r^2/2Dt}$$

↑ This is a Gaussian that spreads out over time:



Because the gaussian spreads out, we can ask on average how far will the solute move from the starting point:

$$\langle r^2(t) \rangle = \int r^2 c(\vec{r}, t)\, d\vec{r}$$

$$= 2d\,Dt$$ ← that is, the root mean square (RMS) displacement increases as $t^{1/2}$

So if we think of each atom as a solute (a point of high concentration @ $t = 0$) we can use the positions of all the particles at a later time to find the diffusion constant

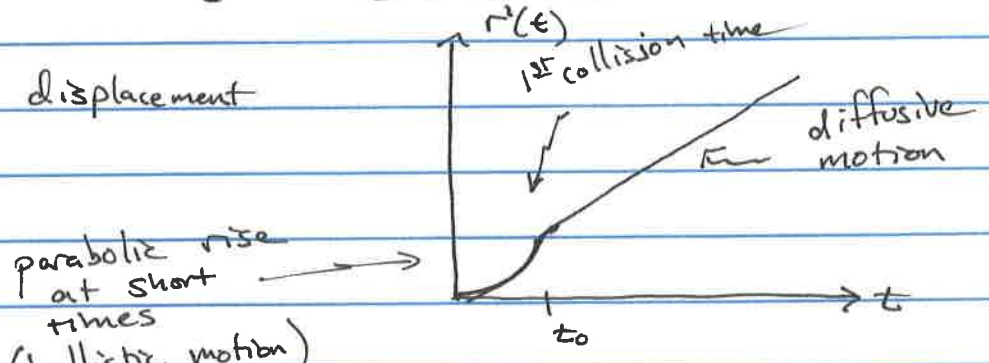
$$D = \lim_{t \to \infty} \frac{1}{2dt} \langle r^2(t) \rangle$$ ← averaged over all the particles

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle |\vec{r}_i(0) - \vec{r}_i(t)|^2 \rangle$$

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} \int_0^{\tau - t} |\vec{r}_i(t') - \vec{r}_i(t'+t)|^2 \, dt'$$

← total length of trajectory

Σ mean square displacement



There's another way of tracking diffusive motion also. Since

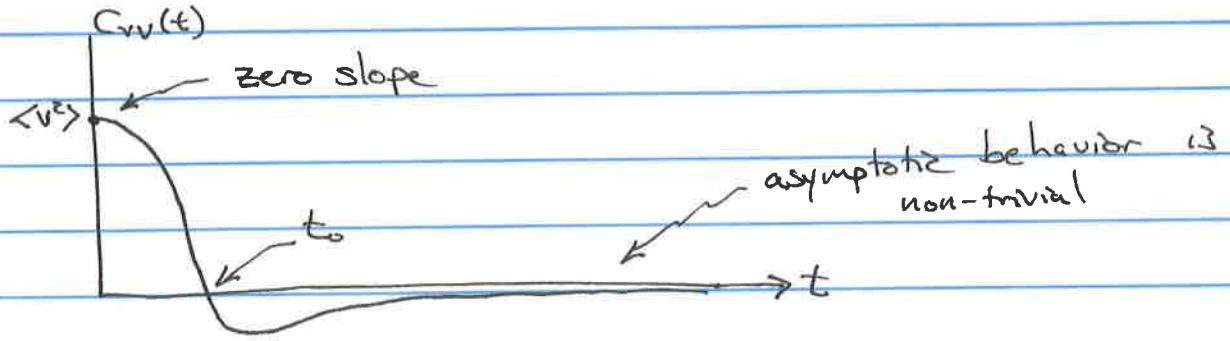
$$\vec{r}(t) = \vec{r}(0) + \int_0^t \vec{v}(t')\,dt'$$

$$\langle r^2(t) \rangle = 2t \int_0^t \langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle\, d\tau = 2dDt$$

velocity autocorrelation function

$C_{vv}(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle$ ← correlates velocity of particles at 2 different times

$C_{vv}(0) = \langle v^2 \rangle = \frac{dk_B T}{m}$



So we really have 2 expressions for the Diffusion constant:

Einstein relation: $D = \lim_{t \to \infty} \frac{1}{2dt} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$

Green-Kubo formula: $D = \frac{1}{d} \int_0^\infty d\tau \langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle$

(Part of lab 3 is figuring out that a slope is easier to compute than an integral)

Other Green-Kubo relations

Shear Viscosity:

$$\eta = \frac{1}{V k_B T} \int_0^\infty \langle \sigma^{xy}(0)\, \sigma^{xy}(t) \rangle dt \qquad \text{with}$$

$$\sigma_{xy} = \sum_{i=1}^{N} \left[m_i v_i^x v_i^y + \frac{1}{2} \sum_{i \neq j} x_{ij} f_y(r_{ij}) \right]$$

(f_y: force in y direction)

$= \sigma_{xy}$ = stress tensor

Thermal Conductivity:

$$\lambda_T = \frac{1}{V k_B T^2} \int_0^\infty \langle q(0) \cdot q(t) \rangle \qquad \text{with}$$

$$q = \frac{d}{dt} \left[\sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 + \frac{1}{2} \sum_{j \neq i} u(r_{ij}) \right]$$

q = heat flux

There are Einstein relations for these also, but they can be noisy:

$$\eta = \lim_{\substack{t \to \infty \\ N \to \infty \\ V \to \infty}} \frac{1}{2 k_B T V t} \left\langle \sum_{i,j=1}^{N} \left[x_i(t) - x_j(0) \right]^2 P_{iy}(t)\, P_{jy}(0) \right\rangle$$

a collective system-wide expression subject to significant noise.